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Adhesive with magnetic nanoparticles

Ans A1

The invention relates to an adhesive comprising magnetic nanoparticles, to processes for its preparation, and to the use of an adhesive comprising nanoparticles.

In a society concerned with preserving raw materials, the reuse of materials is playing an ever greater part. The preservation of renewable raw materials is of particular importance. Within that context, a special position is occupied by the pulp producing and pulp processing industry, which is especially reliant on the renewable raw material wood.

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In order to preserve wood resources, a procedure adopted ever more frequently and with great success in the past has been to recycle waste paper, which contributes significantly to preserving natural cellulose resources. In recycling, waste paper is generally processed to a pulp, bleached where appropriate, and - alone or together with primary pulp from natural cellulose suppliers - is placed on screens, dried and then processed into rolls. A problem with the recycling of waste paper, however, is that its utilization as pulp often leads to problems during the subsequent processing into paper rolls.

Ans A2

Waste paper commonly includes residues of adhesive originating from paper products made using adhesive (books, brochures, sticky notes, and the like) and from papers bonded on the part of users. Where such residues of adhesive are introduced in comminuted form into the processing operation from pulp to paper rolls, the drying of the substantially dewatered pulp may be accompanied by fusion of the residues of adhesive. Where such dried paper webs with fused adhesive residues are subsequently processed to paper rolls on

papermaking and paper processing machines, the fused adhesive residues may cause the paper web to adhere to the production or processing equipment, or may cause sticking of the paper roll itself. Both phenomena may lead to production stoppages and to reduced product quality. In waste paper processing, therefore, the removal of the residues of adhesive (generally referred to as stickies) is very important.

US-A 4 176 054 describes a magnetic hot melt adhesive produced by mixing a ground magnetic substance with the hot melt adhesive in liquid state and then using this hot melt adhesive to bond paper. When, in the course of processing, waste paper bonded with such an adhesive is subjected to a magnetic field, the adhesive-containing portions of the waste paper are said to be separable whereas the non-adhesive-containing constituents may be utilized further, as normal, in the waste paper processing operation. To separate the adhesive-containing fractions of the waste paper it is proposed that the waste paper pieces first be comminuted and then, either in the comminuted state or in a mixture with water, be subjected to a magnetic field.

A problem with the prior art magnetizing methods, however, is that owing to the use of relatively large magnetic particles it is very difficult to achieve particularly homogeneous and finely divided mixing with adhesives. The result, generally, is an inhomogeneous distribution of the magnetic particles in the adhesive.

Where waste paper which has been treated with such an adhesive is to be recycled, it is commonly subjected first to a comminuting process. In the course of this process, the adhesives adhering to the waste paper are also comminuted and may be detached from the paper. As the degree of comminution of the adhesive particles increases, however, there is an increase in the likelihood, owing to the inhomogeneous distribution of

the magnetic particles or because of their size, that individual adhesive particles will no longer contain any magnetic particles. In the magnetic field, such adhesive particles cannot be separated from the remaining waste paper. They are then a cause of the above-described stickies in the production process, which can lead to severe damage and stoppages on the papermaking and paper processing machines.

Often, the intention is not that adhesives should be solid at room temperature in the form of hot melt adhesives; instead, what are desired are liquid adhesives which can be used without high energy consumption on application. Since the solvent based adhesives are unwanted in many countries for ecological reasons, water based dispersion adhesives are a frequently employed alternative here. The use of magnetic particles in dispersion adhesives, however, is difficult, since it is often impossible to incorporate the magnetic particles stably in a dispersion, and phase separation occurs during storage.

It is, accordingly, an object of the present invention to provide an adhesive which does not have the disadvantages of the prior art.

The present invention therefore provides an adhesive comprising at least one polymer and paramagnetic, superparamagnetic or ferromagnetic nanoparticles, or a mixture thereof, having a particle size of from 1 to 1000 nm.

For the purposes of the present invention, an adhesive is a material used for temporary or permanent sticking together of two substrates, especially packaging materials such as paper or cardboard. The term adhesive as used in the context of the present text refers in particular to hot melt adhesives, dispersion adhesives,

pressure sensitive adhesives, hot melt pressure sensitive adhesives, and the like.

For the purposes of the present invention,  
5 nanoparticles are particulate solids which cover a particle size of from about 1 to about 1000 nm, for example from about 2 to about 500 nm, or, for instance, from about 5 to about 300 nm, e.g., about 200 nm or about 30 to about 100 nm. The size figures here refer  
10 to the entirety of the nanoparticles that are present in the adhesive, where at least 90% by weight of the nanoparticles should comply with the abovementioned size figures.

15 The nanoparticles to be used in the context of the present invention have magnetic properties, especially ferromagnetic properties. In one preferred embodiment of the invention, therefore, the nanoparticles comprise at least one element selected from the group consisting  
20 of Fe, Co, Ni, Cr, Mo, W, V, Nb, Ta, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, alloys of two or more of said elements, oxides of said elements or ferrites of said elements, or a mixture of two or more thereof.

25 For example, the nanoparticles may comprise magnetite, machiemite, goethite or ferrite of the general formula  $\text{MeOFe}_2\text{O}_3$ , Me representing an element selected from the group consisting of Mn, Co, Ni, Cu, Zn, Mg or Cd, or a  
30 mixture of two or more thereof.

Also suitable for use as nanoparticles in the context of the present invention are materials such as wolframite ( $\text{FeMnWO}_4$ ), ferberite ( $\text{FeWO}_4$ ), permanent-  
35 magnetic aluminum nickel cobalt alloys, whose principal constituents comprise iron, cobalt, nickel, aluminum, copper or titanium or mixtures of two or more thereof. Also suitable are alloys of platinum and cobalt, alloys of iron, cobalt, vanadium and chromium, ludwigite

- ( $\text{Mg}_2\text{Fe}^{3+}[\text{O}_2/\text{BO}_3]$ ), vonsenite ( $\text{Fe}_2^{2+}\text{Fe}^{3+}[\text{O}_2/\text{BO}_3]$ ), cobalt nickel gravels of the general formula  $\text{A}^{2+}\text{B}^{3+}_2\text{X}^{2-}_4$  in which A stands for iron, cobalt, nickel or copper, B stands for iron, cobalt, nickel or chromium or a mixture of two or more thereof, and X stands for S, Se or Te or a mixture of two or more thereof, iron oxides such as iron(II) oxide ( $\text{FeO}$ ) or iron(III) oxide ( $\text{Fe}_2\text{O}_3$ ) in its ferromagnetic modification,  $-\text{Fe}_2\text{O}_3$  (macchiemite) with spinel, magnetite ( $\text{Fe}_3\text{O}_4$ ), cobalt alloys such as the alloys with a Co-Cr matrix commonly used as high temperature materials, Ni-Fe-Al-Co casting alloys containing up to about 36% by weight cobalt, alloys of the type CoCrW, chromium(IV) oxide ( $\text{CrO}_2$ ), the oxide ceramic materials for classification in the group of the ferrites, of the general composition  $\text{M}^2\text{Fe}_3\text{O}_4$  or  $\text{M}^2\text{O}^*\text{Fe}_2\text{O}_3$ , which contain permanent magnetic dipoles, M representing zinc, cadmium, cobalt, manganese, iron, copper, magnesium and the like, and also iron itself.
- 20 The preparation of magnetite or macchiemite nanoparticles may be achieved, for example, by using a microemulsion technology. Here, the disperse phase of a microemulsion is used to limit the size of the particles that are formed. In a W/O microemulsion, a metal containing reagent is dissolved in the disperse aqueous phase. The reagent is subsequently reacted in the disperse phase to give a precursor of the desired magnetic compound, which thereafter already has the desired size in the nanometer range. Subsequently, with a careful oxidation step, the metal oxide, especially iron oxide in the form of magnetite or macchiemite, is prepared. An appropriate process is described, for example, in US-A 5 695 901.
- 35 Adhesives suitable in the context of the present invention include in particular those adhesives as used to bond paper. Such adhesives commonly include at least one organic synthetic polymer or a natural organic polymer as occurs in nature or may be recovered from

natural substances. Likewise suitable in the context of the present invention are adhesives comprising a mixture of one or more organic synthetic polymers and one or more organic polymers.

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The organic synthetic polymers as used in one preferred embodiment in the context of the present invention include, for example, polyesters, polyethers, polyamides, polyurethanes, polyacrylates, polymeth-  
10 acrylates, polyvinyl acetate, ethylene, vinyl acetate copolymers, propylene-vinyl acetate copolymers, styrene-acrylate and styrene-methacrylate copolymers, and the like.

15 The adhesive of the invention with magnetic nanoparticles may be a hot melt adhesive or a dispersion adhesive in an embodiment as a pressure sensitive adhesive or as a contact adhesive.

20 The adhesive of the invention may be used, for example, as a hot melt adhesive. For the purposes of the present invention, hot melt adhesives are adhesives which at room temperature are solid and are also at least substantially water- and solvent-free. Hot melt  
25 adhesives are applied from the melt to plies of paper that are to be bonded, and on cooling they set physically and solidify. Examples of suitable hot melt adhesives include organic polymers such as polyesters, polyurethanes, polyamides, polyalkylene oxides or  
30 addition polymers, examples being ethylene-vinyl acetate copolymers, or mixtures of two or more of said polymers, or formulations comprising one of said polymers or a mixture of two or more thereof.

35 Polyurethanes, for example, may be used as hot melt adhesive in the context of the present invention.

Polyurethanes as may be used as hot melt adhesive in the context of the present invention are commonly

prepared by reacting at least one polyisocyanate, preferably a diisocyanate, and a polyol component consisting preferably predominantly of diols. The polyol component may contain only one polyol; alternatively, a mixture of two or more different polyols may be used as the polyol component. Polyalkylene oxides, for example, are suitable as the polyol component or at least as part of the polyol component.

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If desired, parts of the polyalkylene oxide may be replaced by other hydrophobic diols containing ether groups and having molecular weights of from 250 to 3000, preferably from 300 to 2000, in particular from 500 to 1000. Specific examples of such diols are polypropylene glycol (PPG), polybutylene glycol, polytetrahydrofuran, polybutadienediol and alkanediols having from 4 to 44 carbon atoms. Preferred hydrophobic diols are polypropylene glycol, polytetrahydrofuran having a molecular weight of from 500 to 1000, and also 1,10-decanediol, 1,12-dodecanediol, 1,12-octadecanediol, dimer fatty acid diol, 1,2-octanediol, 1,2-dodecanediol, 1,2-hexadecanediol, 1,2-octadecanediol, 1,2-tetradecanediol, 2-butene-1,4-diol, 2-butyne-1,4-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol and also its ethoxylation products, especially with up to 30 mol of ethylene oxide.

Besides the diols of the polyol component, diisocyanates are key building blocks of the polyurethane which can be used as hot melt adhesive. These are compounds of the general structure  $O=C=N-X-N=C=O$ , X being an aliphatic, alicyclic or aromatic radical, preferably an aliphatic or alicyclic radical having from 4 to 18 carbon atoms.

Examples that may be mentioned of suitable isocyanates include 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), hydrogenated MDI ( $H_{12}$ MDI),



xylylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), 4,4'-diphenyldimethylmethane diisocyanate, di- and tetraalkylenediphenylmethane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers of tolylene diisocyanate (TDI), 1-methyl-2,4-diisocyanatocyclohexane, 1,6-diisocyanato-2,2,4-trimethylhexane, 1,6-diisocyanato-2,4,4-trimethylhexane, 1-isocyanatomethyl-3-isocyanato-1,5,5,-trimethylcyclohexane (IPDI), chlorinated and brominated diisocyanates, phosphorus diisocyanates, 4,4'-diisocyanatophenylperfluoroethane, tetramethoxybutane 1,4-diisocyanate, butane 1,4-diisocyanate, hexane 1,6-diisocyanate (HDI), dicyclohexylmethane diisocyanate, cyclohexane 1,4-diisocyanate, ethylene diisocyanate, bisisocyanatoethyl phthalate, and also diisocyanates containing reactive halogen atoms, such as 1-chloromethylphenyl 2,4-diisocyanate, 1-bromomethylphenyl 2,6-diisocyanate, 3,3-bis-chloromethyl ether 4,4'-diphenyl diisocyanate.

20 Sulfur polyisocyanates are obtained, for example, by reacting 2 mol of hexamethylene diisocyanate with 1 mol of thiodiglycol or dihydroxydihexyl sulfide. Further diisocyanates that may be used are, for example, 25 trimethylhexamethylene diisocyanate, 1,4-diisocyanatobutane, 1,12-diisocyanatododecane, and dimer fatty acid diisocyanate. The following are especially suitable: tetramethylene, hexamethylene, undecane, dodecamethylene, 2,2,4-trimethylhexane, 1,3-cyclohexane, 1,4-cyclohexane, 1,3- and/or 1,4-tetramethylxylylene, 30 isophorone, 4,4-dicyclohexylmethane, and lysine ester diisocyanate. Very particular preference is given to tetramethylxylylene diisocyanate (TMXDI), especially the m-TMXDI from Cyanamid.

35 To further increase the molecular weight it is possible, for example, to perform a chain extension in a known manner. For this purpose, prepolymers are prepared first of all using excess diisocyanate, and

are then extended using short-chain amino alcohols, diols or diamines or using water, with an increase in the molecular weight.

5 Preferably, however, the polyurethane is prepared in a single stage process. In this case, for example, first all of the starting materials are mixed in the presence of an organic solvent, with a water content of less than 0.5% by weight. The mixture is heated at from 80  
10 to 200°C, in particular at from 100 to 180°C and preferably at from 130 to 170°C, for from about 1 to 30 hours. The reaction time may be shortened by the presence of catalysts. In particular it is possible to use tertiary amines, e.g., triethylamine,  
15 dimethylbenzylamine, bisdimethylaminoethyl ether and bismethylaminomethylphenol. Particularly suitable are 1-methylimidazole, 2-methyl-1-vinylimidazole, 1-allylimidazole, 1-phenylimidazole, 1,2,4,5-tetramethylimidazole, 1-(3-aminopropyl)imidazole, pyrimidazole, 4-di-  
20 methylaminopyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine or 4-methylpyridine. It is preferred, however, to work without a catalyst. The solvent as well is appropriately omitted. By solvents in the context of the present text are meant inert organic  
25 liquid substances having a boiling point of less than 200°C under atmospheric pressure.

If the adhesive of the invention is to be a dispersion adhesive, then in one preferred embodiment it comprises  
30 an organic synthetic polymer selected from the group consisting of polyacrylates, polymethacrylates, polystyrene, polyvinyl esters, ethylene-vinyl acetate copolymers or acrylate-styrene copolymers.

35 In another preferred embodiment of the invention, the adhesive of the invention is a dispersion adhesive.

Instead or in addition to one or more organic synthetic polymers the adhesive of the invention may comprise an

organic natural polymer or a mixture of two or more thereof. By an organic natural polymer are meant polymers as may be obtained from natural substances by simple chemical operations. In the context of the present invention, the term also includes simple derivatives of organic natural polymers, examples being the esterification derivatives or alkoxylation derivatives of starch or of cellulose.

10 In one preferred embodiment of the present invention, the adhesive of the invention contains the nanoparticles in an amount of from about 0.1 to about 50% by weight, preferably in an amount of from about 1 to about 30% by weight, in particular from about 2 to  
15 about 20% by weight.

The adhesive of the invention contains the organic synthetic polymer or the organic natural polymer or the mixture of one or more organic synthetic polymers and one or more organic natural polymers in an amount of at least about 10% by weight. If the adhesive of the invention is to be used as a hot melt adhesive, then it is advantageous if it contains at least one synthetic organic polymer or one natural organic polymer in a  
20 relatively large amount, for example, at least about 50% by weight.

Likewise suitable as adhesives in the context of the present invention are hot melt adhesives containing  
30 postcrosslinking groups, as are commonly used to produce bonds possessing particular heat stability. In this context, the use of polyurethanes as synthetic organic polymer is particularly appropriate.

35 The adhesive of the invention may further comprise a heat sealing adhesive. By heat sealing adhesives are meant heat activatable adhesives which are applied as a solution, emulsion, dispersion or melt to the surface of the substrates to be sealed. There, initially owing

to the evaporation of the solvents or by cooling, they set to give a nontacky adhesive film. The subsequent bonding of the substrates generally takes place, following their joining and pressing together, by heating in hot presses or in a high frequency field. On cooling, the workpieces are bonded with solidification of the heat sealing adhesive film. Especially suitable for use in heat sealing adhesives are, for example, copolymers based on ethylene, (meth)acrylates, vinyl chloride, vinylidene chloride, vinyl acetate, and also polyamides, polyesters and polyurethanes.

The adhesive of the invention may further comprise a pressure sensitive adhesive. Pressure sensitive adhesives are generally viscoelastic adhesives which in solvent-free form at 20°C are permanently tacky and remain adherable, and, with low substrate specificity, adhere immediately to virtually all substrates under gentle applied pressure. Bonds produced using pressure sensitive adhesives can usually be parted without destroying the bonded substrates. In the context of the present invention, pressure sensitive adhesives comprise as organic synthetic polymer, for example, natural and synthetic rubbers, polyacrylates, polyesters, polychloroprenes, polyisobutenes, polyvinyl ethers and polyurethanes. If desired, the pressure sensitive adhesives may further comprise additives which promote, for example, one-sided redetachability from paper surfaces.

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In another preferred embodiment of the invention, the adhesive of the invention is a dispersion adhesive. Adhesives termed dispersion adhesives are mostly aqueous dispersions of organic polymers which are capable of bonding wood, paper, cardboard, wall coverings, leather, felt, cork, textiles, plastics or metals. Dispersion adhesives set by evaporation of the dispersion medium (water) to form an adhesive film. Examples of suitable synthetic organic polymers in

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- 12 -

dispersion adhesives are polyacrylates, poly-methacrylates, polyurethanes, polyesters, polyvinyl acetals, ethylene-vinyl acetate (EVA) copolymers, and the like.

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In addition to the abovementioned organic synthetic or natural polymers, the adhesive of the invention may comprise further additives which influence, for example, the sticking properties, the aging behavior, the setting process, or the adhesion. For example, the adhesive may include what are known as tackifier resins, which can generally be subdivided into natural and synthetic (synthetic resins). They include, for example, alkyd resins, epoxy resins, melamine resins, phenolic resins, urethane resins, hydrocarbon resins, and also natural resins such as rosin, wood terpentine oil and tall oil. The synthetic resins include hydrocarbon resins, ketone resins, coumarone-indene resins, isocyanate resins, and terpene phenolic resins.

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Furthermore, adhesives of the invention may comprise solvents. Examples of suitable solvents are mono or polyhydric alcohols having from about 2 to about 10 carbon atoms.

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Additionally, the adhesives of the invention may comprise defoamers. Examples of suitable defoamers are fatty alcohol based or silicone based defoamers.

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The adhesives may additionally comprise protective colloids such as polyvinylpyrrolidones, polyvinyl alcohols, cellulose or cellulose derivatives.

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Additives which the adhesive of the invention may further comprise include stabilizers or antioxidants. Included among these, generally, are phenols, sterically hindered phenols of high molecular weight, polyfunctional phenols, sulfur and phosphorus containing phenols or amines. Examples of suitable

stabilizers include hydroquinone, hydroquinone methyl ether 2,3-(di-tert-butyl)hydroquinone, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene; pentaerythritol tetrakis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; n-octadecyl 3,5-di-tert-butyl-4-hydroxyphenyl)propionate; 4,4-methylenebis(2,6-di-tert-butylphenol); 4,4-thiobis(6-tert-butyl-o-cresol); 2,6-di-tert-butylphenol; 6-(4-hydroxyphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine; di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonates; 2-(n-octylthio)-ethyl-3,5-di-tert-butyl-4-hydroxybenzoate; and sorbitol hexa[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]; and also p-hydroxydiphenylamine or N,N'-diphenylenediamine or phenothiazine.

The adhesive of the invention may further comprise plasticizers such as benzoate plasticizers, phosphate plasticizers, liquid resin derivatives or vegetable and animal oils. Suitable examples include sucrose benzoate, diethylene glycol dibenzoate and/or diethylene glycol benzoate in which from about 50 to about 95% of all hydroxyl groups have been esterified, phosphate plasticizers, for example, t-butylphenyl diphenyl phosphate, polyethylene glycols and their derivatives, for example, diphenyl ethers of poly(ethylene glycol), liquid resin derivatives, for example, the methyl esters of hydrogenated resin, vegetable and animal oils, for example, glycerol esters of fatty acids and their polymerization products.

Likewise suitable are plasticizers based on phthalic acid, especially the alkyl phthalates.

The adhesive of the invention may further comprise dyes such as titanium dioxide, fillers such as talc, clay and the like, and also pigments.

Where the adhesive of the invention comprises an adhesive which is postcrosslinking, for example,

through the influence of electron beams or UV rays it is possible for photoinitiators to be present as additional additives in the adhesive. Said photoinitiators may, for example, comprise Norrish type

5 I fragmenting substances such as benzophenone, hydroquinone, photoinitiators of the Irgacure<sup>®</sup>, Darocure<sup>®</sup> or Speedcure<sup>®</sup> range (manufacturer: Ciba-Geigy). If desired, the adhesive of the invention may comprise a monofunctional reactive diluent which is

10 polymerizable, for example, by irradiation with UV light or with electron beams. Particularly suitable for this purpose are the corresponding esters of acrylic acid or methacrylic acid. Example of such esters include N-butyl acrylate, 2-ethylhexyl acrylate,

15 3-methoxybutyl acrylate, 2-phenoxyethyl acrylate, benzyl acrylate or 2-methoxypropyl acrylate.

The adhesives of the invention may further comprise emulsifiers or stabilizers or a mixture thereof.

20 Suitable emulsifiers are generally surfactants which have a hydrophilic and a hydrophobic group. These may be anionic emulsifiers, cationic emulsifiers or amphoteric emulsifiers. Suitable examples include hydrocarbon emulsifiers containing from about 6 to

25 about 22 carbon atoms, the hydrocarbon chain being branched, unbranched, saturated, unsaturated, substituted, aliphatic or aromatic.

For the preparation of the adhesives of the invention,

30 the organic synthetic polymer or the organic natural polymer or the mixture of one or more organic synthetic polymers and one or more organic natural polymers are mixed with the nanoparticles and, if desired, with a solvent and further additives. If the adhesive of the

35 invention is to be a hot melt adhesive, then mixing may take place in the melt of the hot melt adhesive; however, it is likewise possible to add the nanoparticles as early as during the preparation of the polymer which is used as the hot melt adhesive.

Where the adhesive of the invention is to be a dispersion adhesive, the nanoparticles may be incorporated directly into the polymer dispersion of  
5 the dispersion adhesive.

In another preferred embodiment of the invention, the nanoparticles are added to a dispersion adhesive of the invention even before the preparation of the synthetic  
10 organic polymer. In this case the dispersion adhesive of the invention is prepared by means of an emulsion polymerization in the course of which, customarily, droplets of monomers needed to prepare the subsequent polymer are polymerized in an aqueous emulsion. The  
15 nanoparticles may be added to the emulsion even before the polymerization, leading to a particularly homogeneous distribution of the nanoparticles in the dispersion adhesive.

20 In a further preferred embodiment of the present invention, the nanoparticles are directly attached ionically, coordinatively or covalently to an organic synthetic or organic natural polymer.

25 For this purpose the nanoparticles are surface modified in such a way that, subsequently, a reaction with a functional group of an organic natural or synthetic polymer is possible or it is possible for the modified nanoparticle to be incorporated into an organic  
30 synthetic polymer.

In one preferred embodiment of the invention, the surface of the nanoparticles is modified, for example, with silanes. Where oxides are used as nanoparticles,  
35 these oxides generally carry surface OH groups which are able to react with silanes or halosilanes to form a covalent Si-O bond. If the silanes, for their part, possess an appropriate functional group which permits subsequent attachment of the silanes to a polymer, this



may be used to affix the modified nanoparticles covalently to the polymer. Suitable functional groups are, for example, olefinically unsaturated double bonds or protected OH or NH groups. An appropriate  
5 possibility for modifying the surface of nanoparticles with silane compounds is described, for example, in US-A 5,695,901.

The invention additionally provides a process for  
10 preparing an adhesive, characterized in that a polymer, paramagnetic or ferromagnetic nanoparticles or a mixture thereof and, where appropriate, solvents or further additives or a mixture of two or more thereof are mixed.

15 The present invention likewise provides for the use of paramagnetic or ferromagnetic nanoparticles or of a mixture of one or more paramagnetic and one or more ferromagnetic nanoparticles having a particle size of  
20 from about 10 to about 300 nm in adhesives.